

Advanced Microscopies of Next- Generation Lithium-Ion Battery Cathode Materials

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Overview

Timeline

- Start date: Oct. 1, 2018
- End date: Sept. 30, 2021
- Percent complete: 50%

Budget

- Total project funding
- DOE share: \$450 (2019)
- Funding received in FY 2020: \$600k

Barriers addressed

- Fading and failure mechanism of next-generation cathode
- Identify critical factors that control the properties of next-generation cathode

Partners

- Lawrence Berkeley National Laboratory
- Argonne National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Battery group at Pacific Northwest National Laboratory



Relevance

- ▶ This characterization endeavor is to probe the structural and chemical evolution of the next-generation cathode materials. It is relevant to the cathode deep-dive effort, targeting to delineate at atomic and electronic levels on factors that critically control the performance of the cathode materials.
- ▶ Electrochemical properties of cation-disordered rock cathode is closely related to the structural and chemical evolution of the cathode upon cycling. Revealing atomic-scale structural and chemical evolution will provide insight for designing better cathode materials.
- ▶ During the material optimization process, electron microscopic characterization will be fully integrated into each step of the process for understanding the effects of different process parameters on the capacity and long-term stability of modified cathode materials.
- ▶ Both ex-situ and *in situ* TEM will be used to directly observe the characteristics of the layer-based cathode materials and the electrolyte interface structures and chemistry with respect to surface coatings.

Milestones

- ▶ Reveal the structural and chemical nature of short-range order in the cation-disordered rock-salts cathode; establish the grain boundary mediate mass transport on the stability of low-Co concentration cathode (12/31/2019, complete)
- ▶ Determine the evolution of the short-range order on battery cycling; establish the lattice structural stability of the low-Co cathode with surface, lattice, and electrolyte modifications (03/31/2020, complete)
- ▶ Reveal the correlation of structural and chemical evolution of low-Co cathode with electrochemical properties (06/30/2020, on track)
- ▶ Determine the controlling factors that affect the stability of low-Co cathode in contact with liquid electrolyte (09/30/2020, on track)



Approach

- ▶ To get insights into the structural and chemical information at atomic resolution, aberration-corrected STEM-HAADF atomic-level imaging combined with atomic level EDS chemical analysis and EELS on atomic-level electronic structure will be used to probe the microstructural, chemical and electronic evolution of the cathode before and after the electrochemical cycling.
- ▶ EELS and EDS mapping will be used to explore the elemental distribution both within the bulk lattice and at the particle surface to gain information of local structures and the interaction of electrolyte and cathode in the structure and chemistry of solid electrolyte interphase layer.
- ▶ Direct correlation of the structural and chemical information with battery properties will provide insight on the capacity degradation mechanism of both cation-disordered rock-salt structured materials and Co-free cathode with different compositions, substitution, and surface modification.
- ▶ This characterization task will be closely integrated with the materials development and modeling tasks for guiding the designing of next-generation cathode materials toward high-performance cathode.

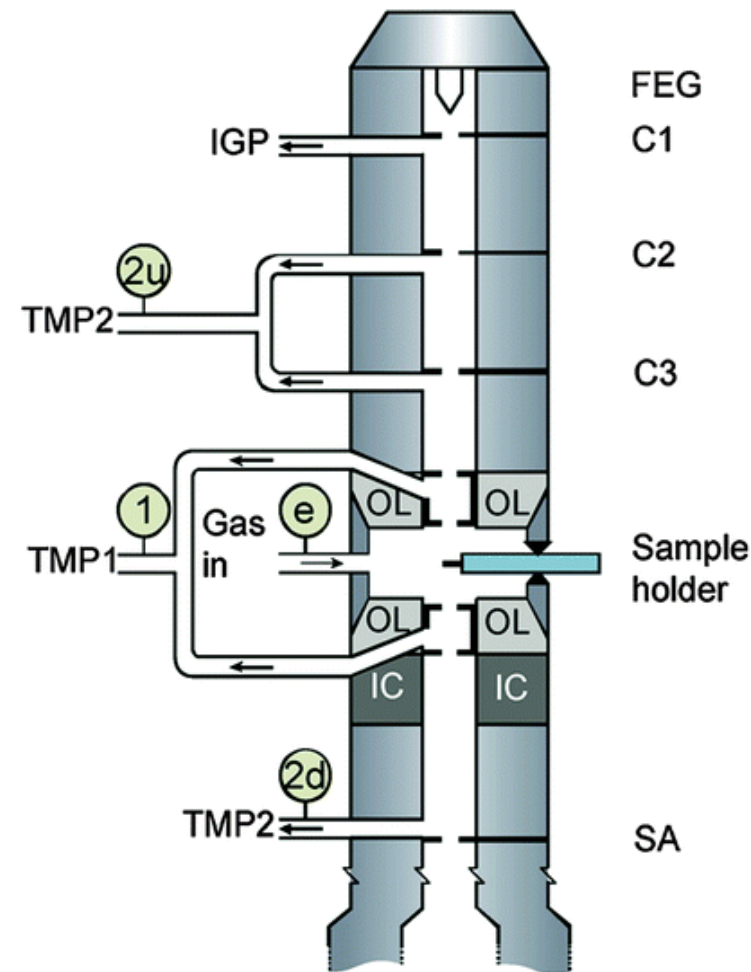
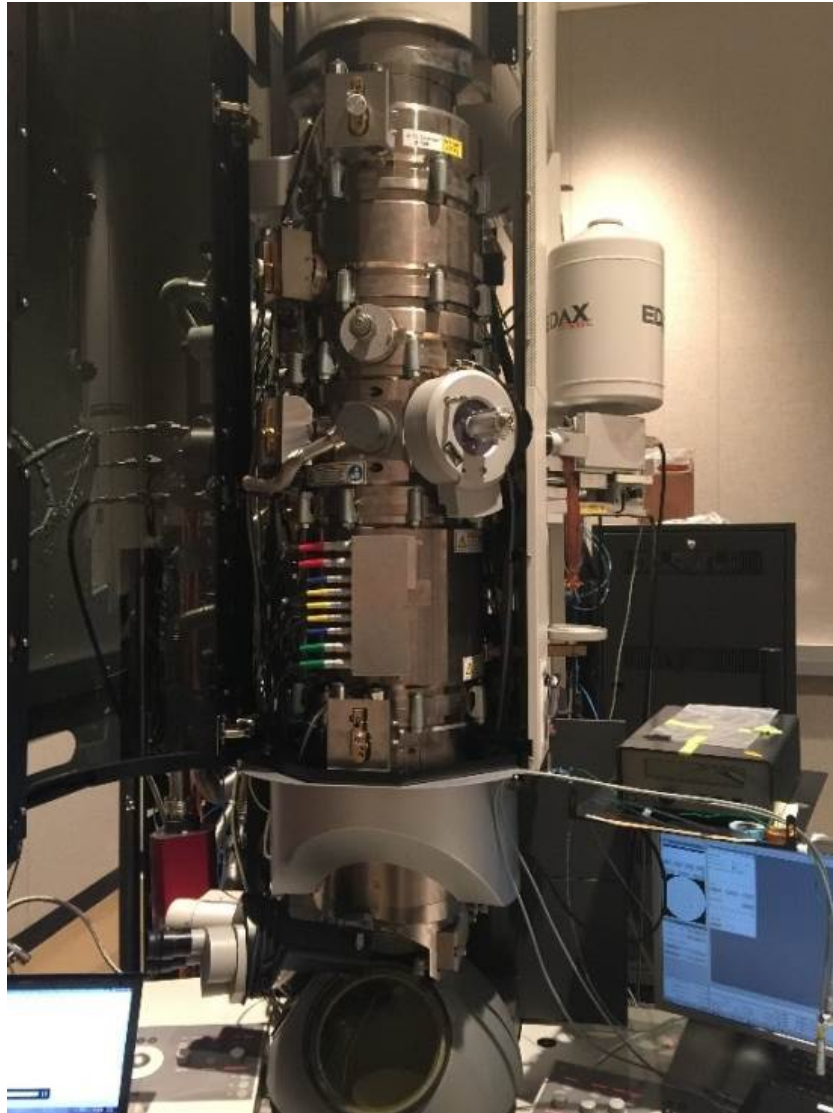


Technical Accomplishments and Progress

- ▶ Revealed the nature of the ordering in DRX: short-range order, meso-scale order, and long-range order
 - Discovered the meso-scale ordering in DRX
 - Established correlations among fabrication, ordering, and electrochemical properties for DRX
- ▶ Using *in situ* TEM, revealed the nature of the cathode-air interfacial reaction and its dependence on Ni concentration
 - Revealed that the water-vapor-induced delithiation is the governing factor for controlling the surface passivation of layered cathode
 - Revealed that the surface passivation layer has a critical thickness, which depends on the surface reconstruction layer thickness
- ▶ Revealed the correlation of secondary cathode particle structure and the surface phase transition layer thickness
 - Direct contacting with liquid electrolyte leads to interfacial and bulk lattice instability
- ▶ Revealed the functioning mechanism of dopants, such as Zr and W in enhanced cycling stability of low Co and Co-free layer structured cathode

Technical Accomplishments

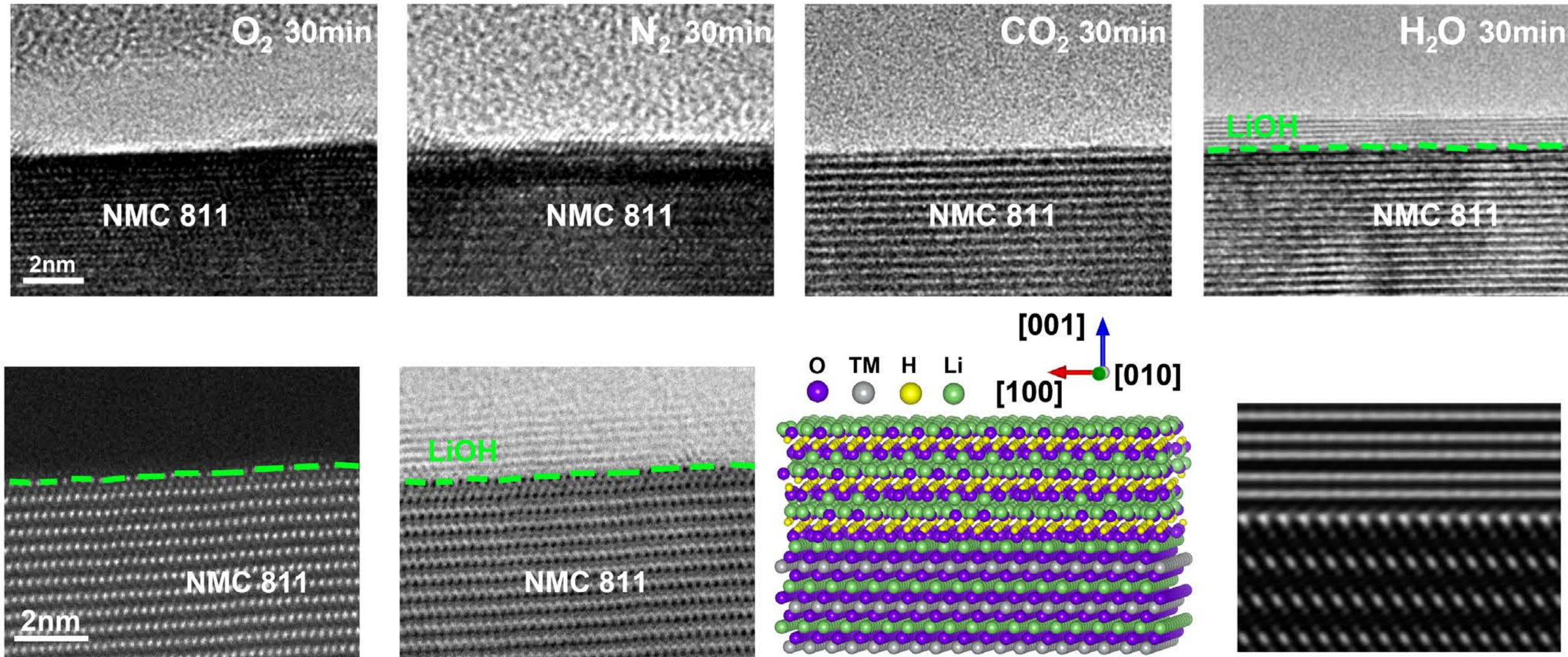
***In situ* and environmental TEM to reveal the true nature of the air-sensitivity of NMC cathode**



- ▶ Controlled gas environment to enable the *in situ* observation of surface reaction, typically includes H_2O , O_2 , N_2 , and CO_2
- ▶ To study the thermal properties of the cathode, the temperature of the *in situ* TEM can be controlled up to 1000.
- ▶ Integrated cryo-TEM capability enables study of beam-sensitive battery materials, such as the cathode electrolyte interphase layer.

Technical Accomplishments

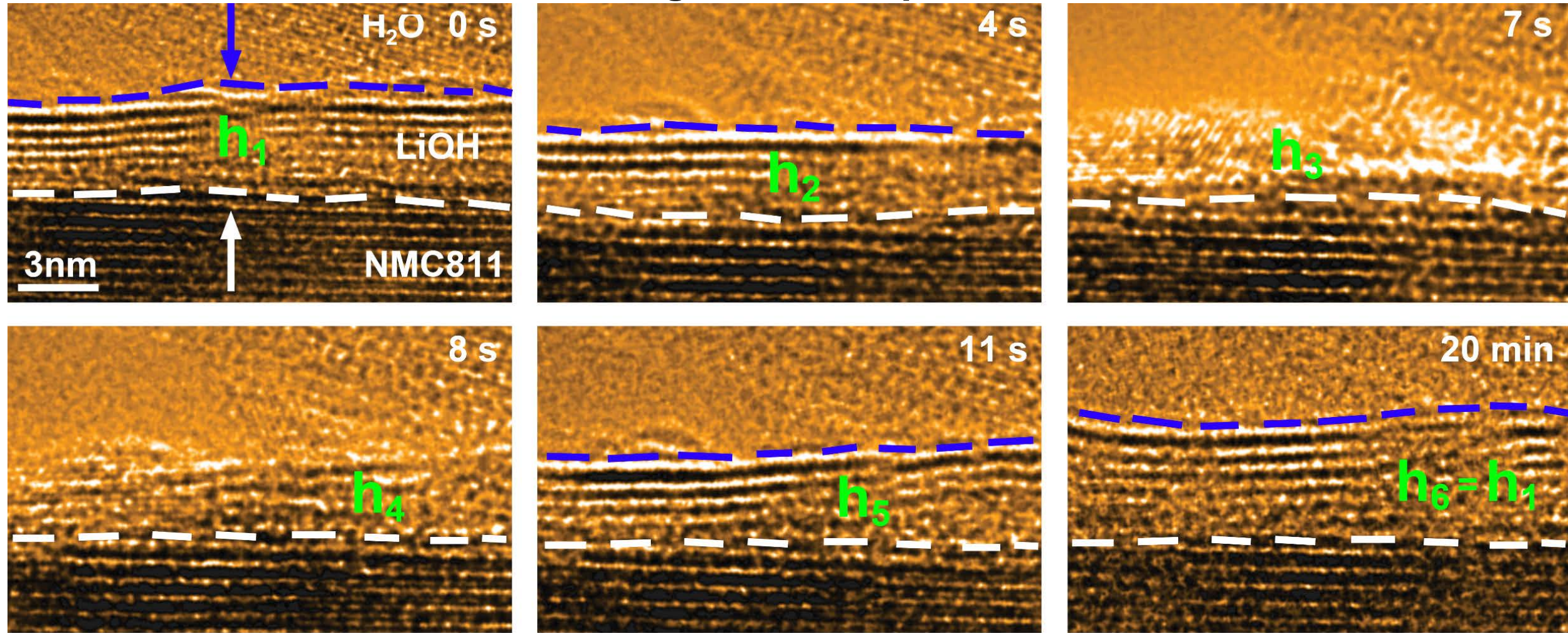
Unlocking the nature of the cathode-air interfacial reaction in lithium ion batteries



- ▶ To reveal the nature of the surface sensitivity of cathode in air, using *in situ* TEM to probe the response of freshly exposed surface of NMC with H_2O vapor, O_2 , N_2 , CO_2 to isolate the reaction mechanism.
- ▶ H_2O vapor is the only species in air that can trigger the chemical delithiation of the NMC cathode and lead to the surface passivation

Technical Accomplishments

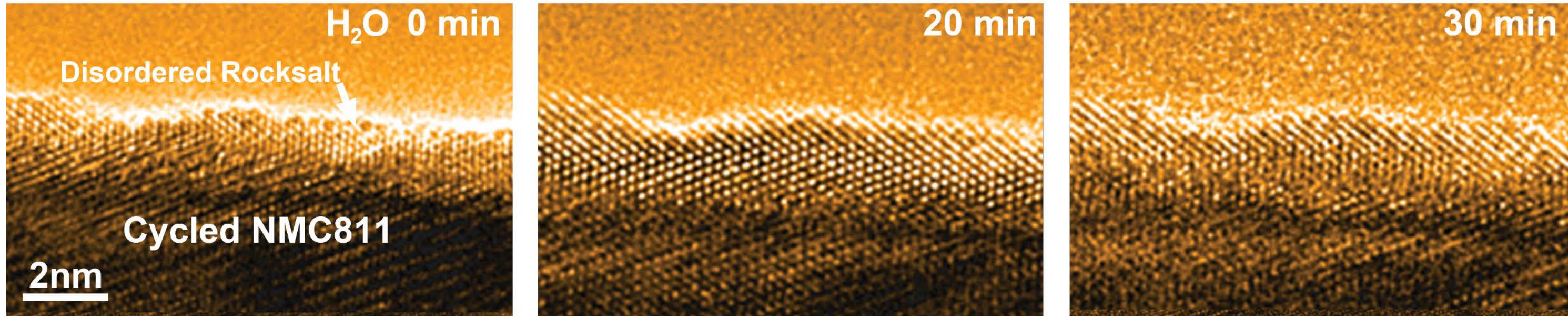
Self-healing of surface passivation



- ▶ Using electron beam to remove the surface passivation layer, then it grows back.
- ▶ The surface passivation layer shows a feature of self-healing to critical thickness.

Technical Accomplishments

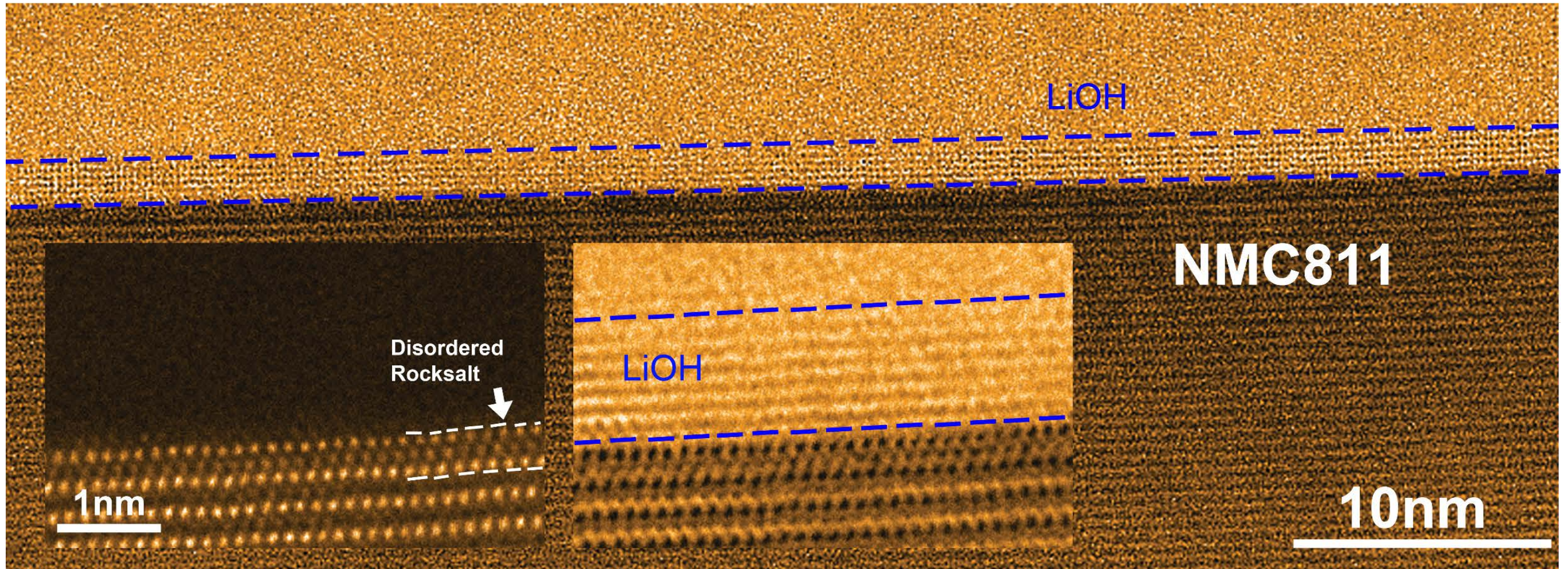
The surface passivation layer shows dependence on the thickness of the surface reconstruction layer



- ▶ Controlling the surface structure to block Li delithiation can lead to the control of the surface passivation layer thickness.
- ▶ The surface reconstruction layer, such as rock-salt phase, can effectively reduce the surface passivation layer thickness.

Technical Accomplishments

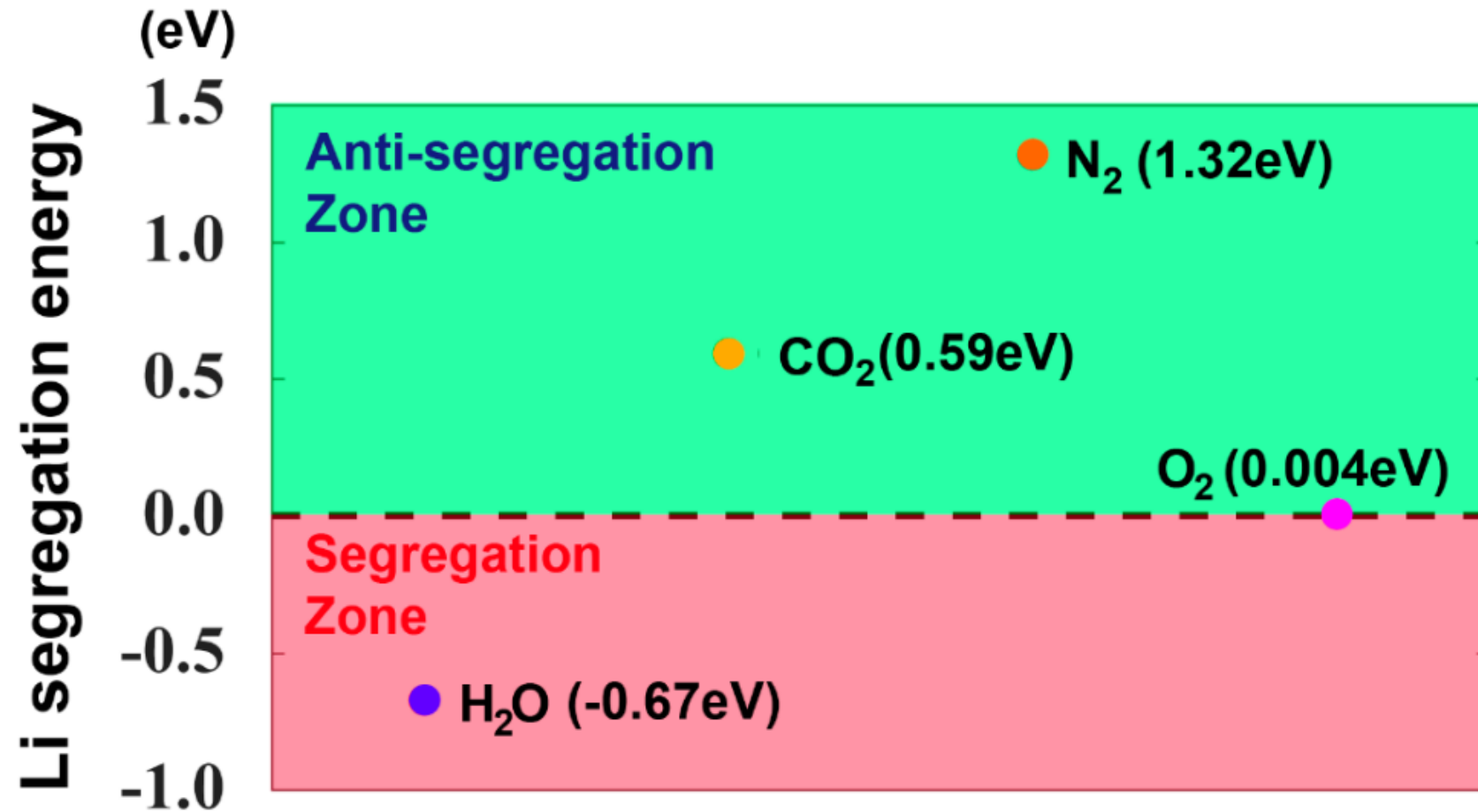
The surface passivation layer shows dependence on the thickness of the surface reconstruction layer



- ▶ A thin layer of rocksalt phase on the surface is not enough to block delithiation, leading to a surface passivation layer of 2 nm.

Technical Accomplishments

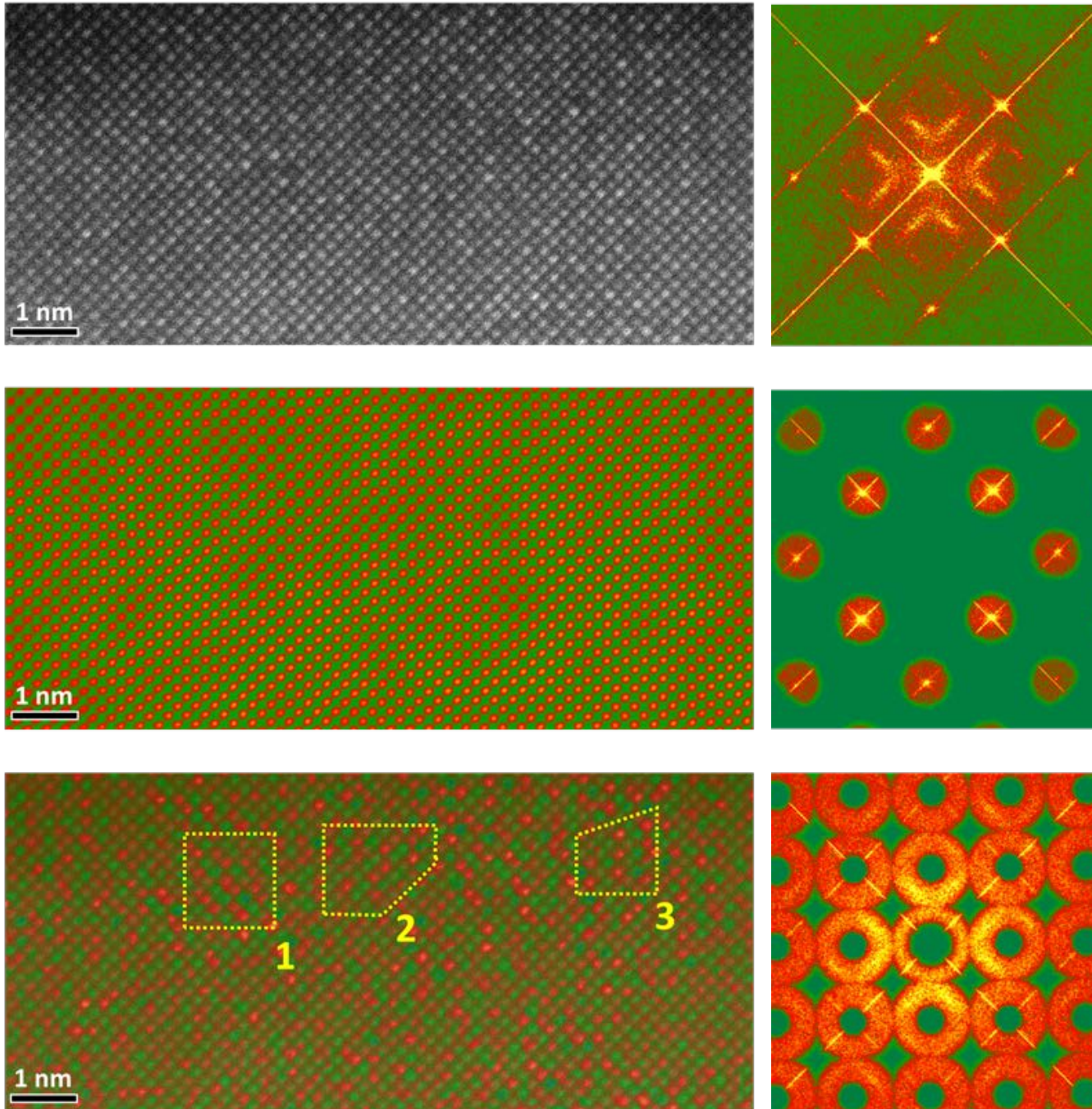
Li segregation energies derived based on DFT calculation for the adsorption of different gases



- ▶ Water-vapor-driven Li de-intercalation is the critical step to control the surface reaction product.
- ▶ Delithiation of Li and reaction with water vapor leads to the formation of LiOH.
- ▶ The kinetics of surface reactions reveal a critical thickness of the reaction product, a feature of the passivating nature of the LiOH.
- ▶ The critical thickness shows dependence on Ni concentration, increases with the increase of the Ni concentration

Technical Accomplishments

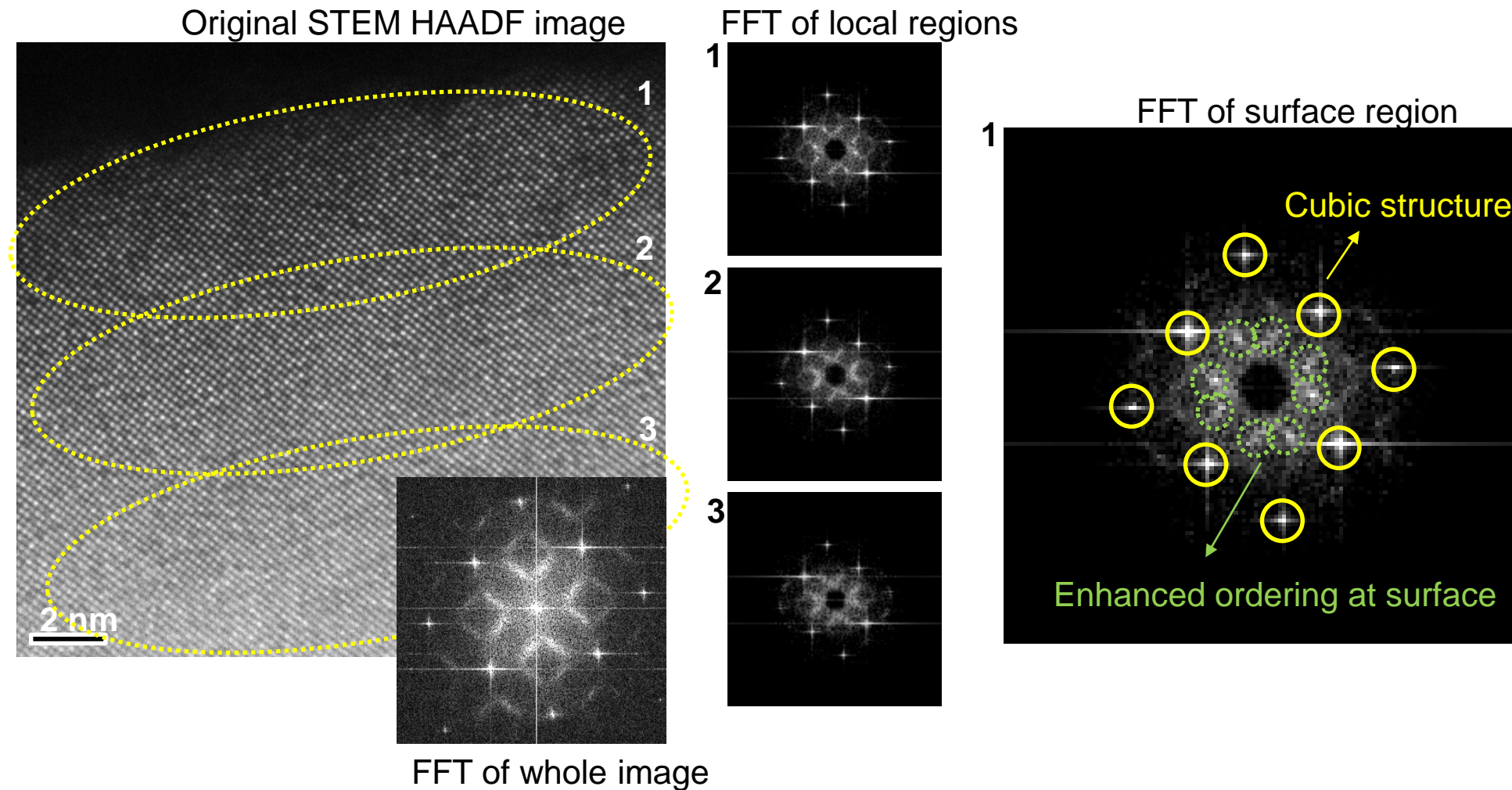
Cation ordering in DRX materials LTMOF ($\text{Li}_{1.2}\text{Ti}_{0.2}\text{Mn}_{0.6}\text{O}_{1.8}\text{F}_{0.2}$)



- ▶ By using FFT-filtering techniques based on atomic-resolution STEM imaging, atomic arrangements corresponding to diffuse scattering intensity in reciprocal space can be directly extracted.
- ▶ Quasi-periodic patterns of atomic distributions across long ranges are observed, resembling a transitional ordering state between short-range order and long-range order.
- ▶ These ordering patterns should be correlated to the Li-percolation channels.

Technical Accomplishments

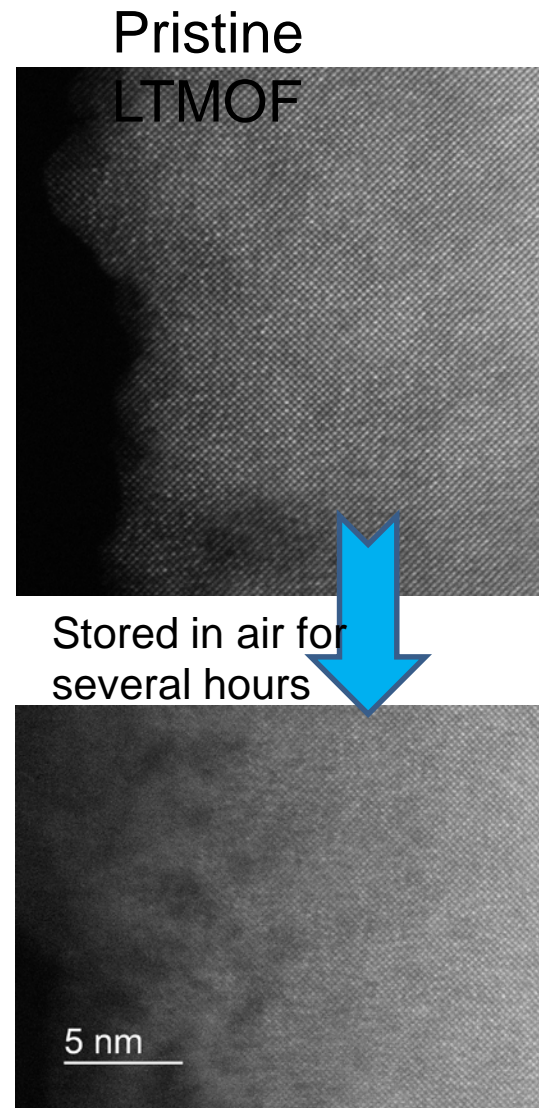
Atomic-scale ordering enhancement at surfaces of $\text{Li}_{1.2}\text{Ti}_{0.2}\text{Mn}_{0.6}\text{O}_{1.8}\text{F}_{0.2}$



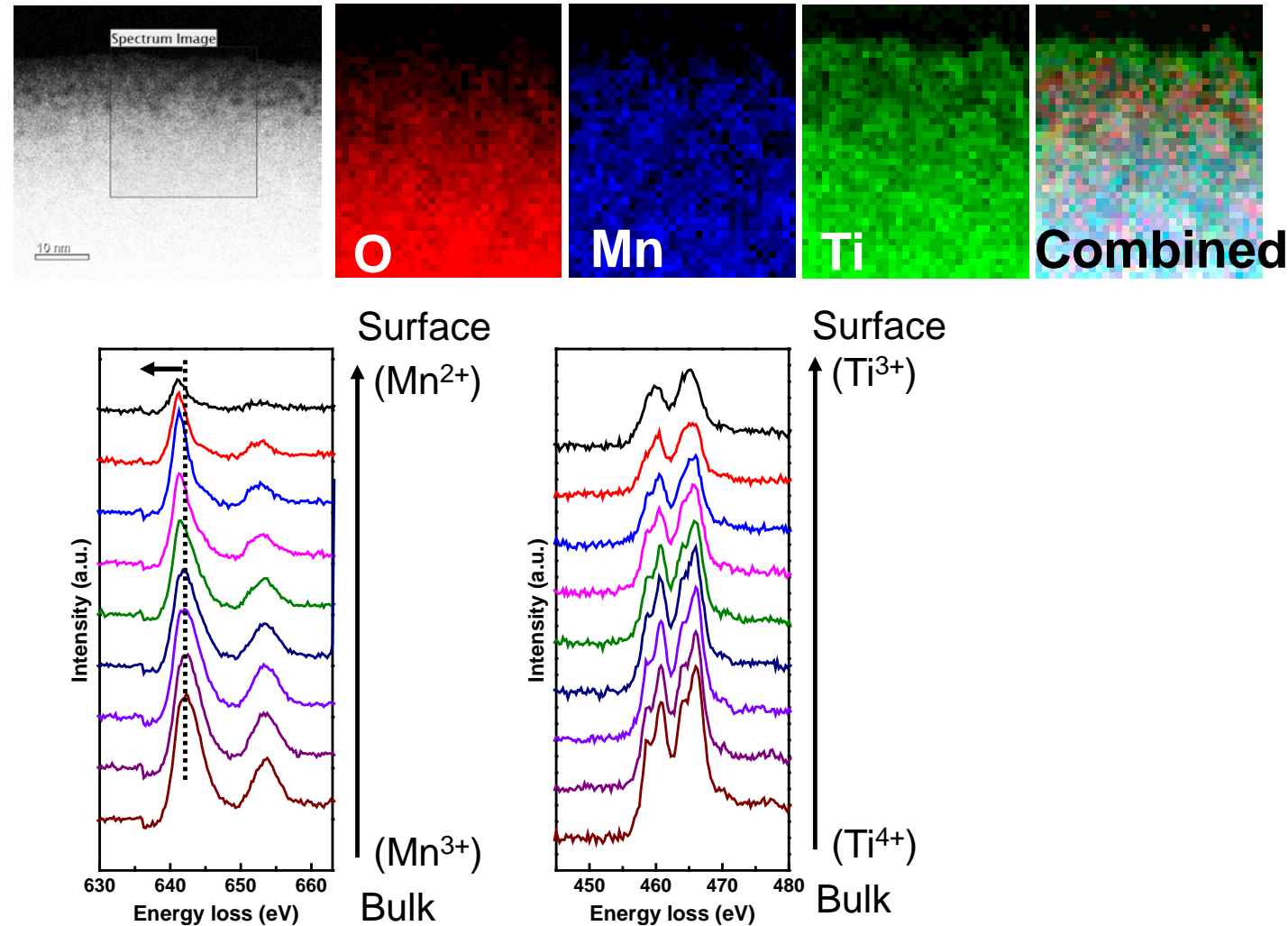
- ▶ Spatial distribution of short-range order plays a big role in the electrochemical properties of DRX.
- ▶ The short-range order shows spatial difference from particle surface to the interior of the particle.
- ▶ The particle surface shows enhanced atomic-scale ordering at the surface layer (~ 5 nm thin).

Technical Accomplishments

Surface stability of $\text{Li}_{1.2}\text{Ti}_{0.2}\text{Mn}_{0.6}\text{O}_{1.8}\text{F}_{0.2}$ upon exposure in air



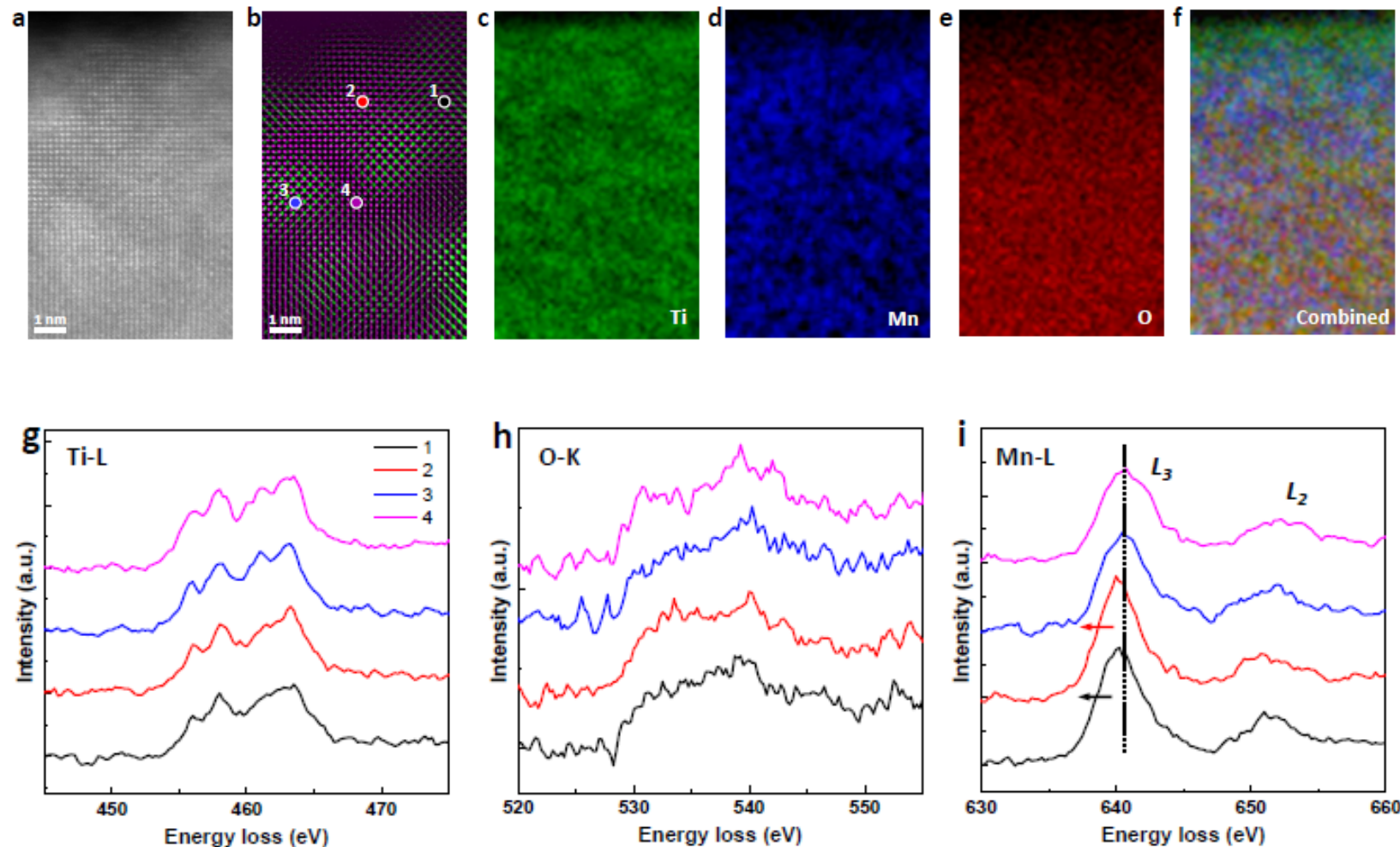
Reacted surface of LTMOF



- ▶ EELS maps show O and Mn are depleted at the outmost surface, while Ti is retained.
- ▶ When approaching from the bulk to the surface, reduction of oxidation states are observed for both Ti and Mn.
- ▶ The nature of the surface air sensitivity needs further exploration.

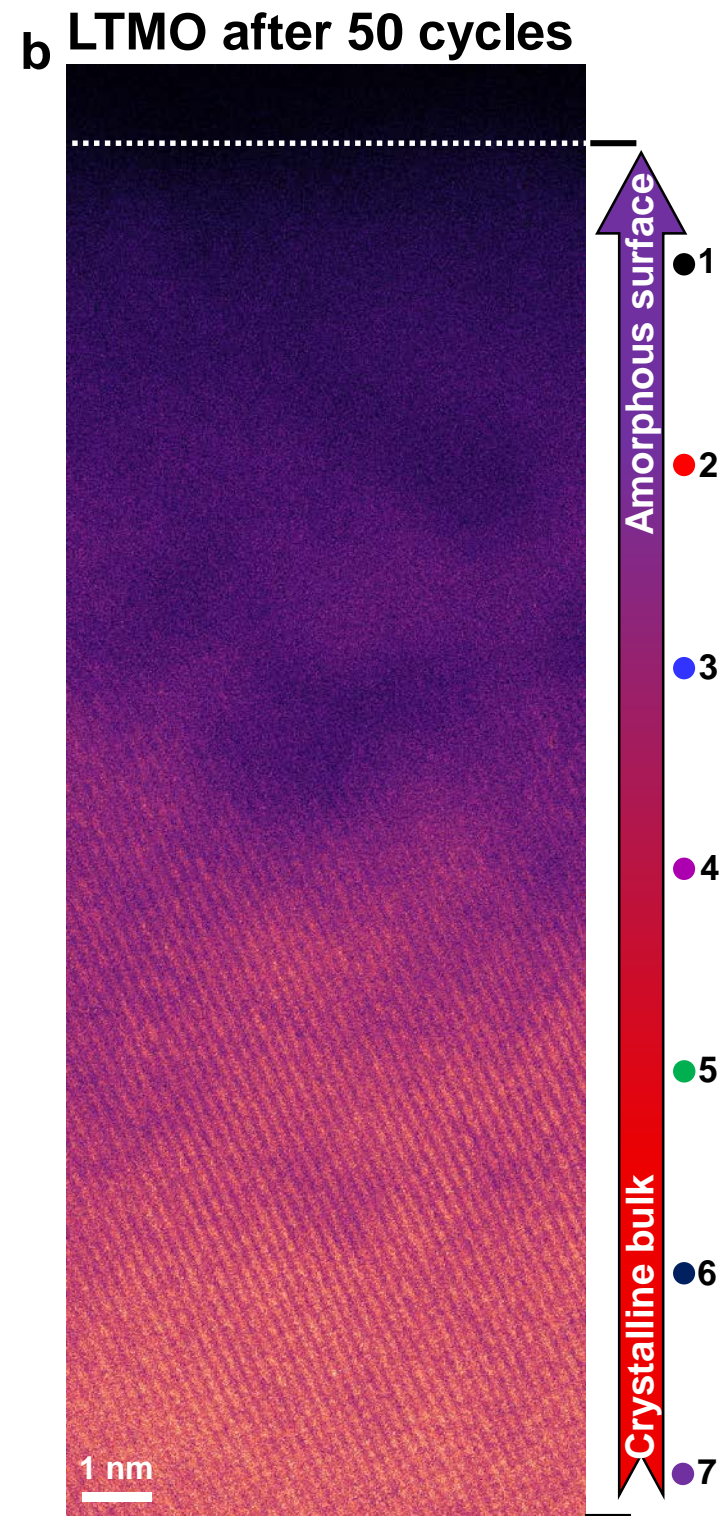
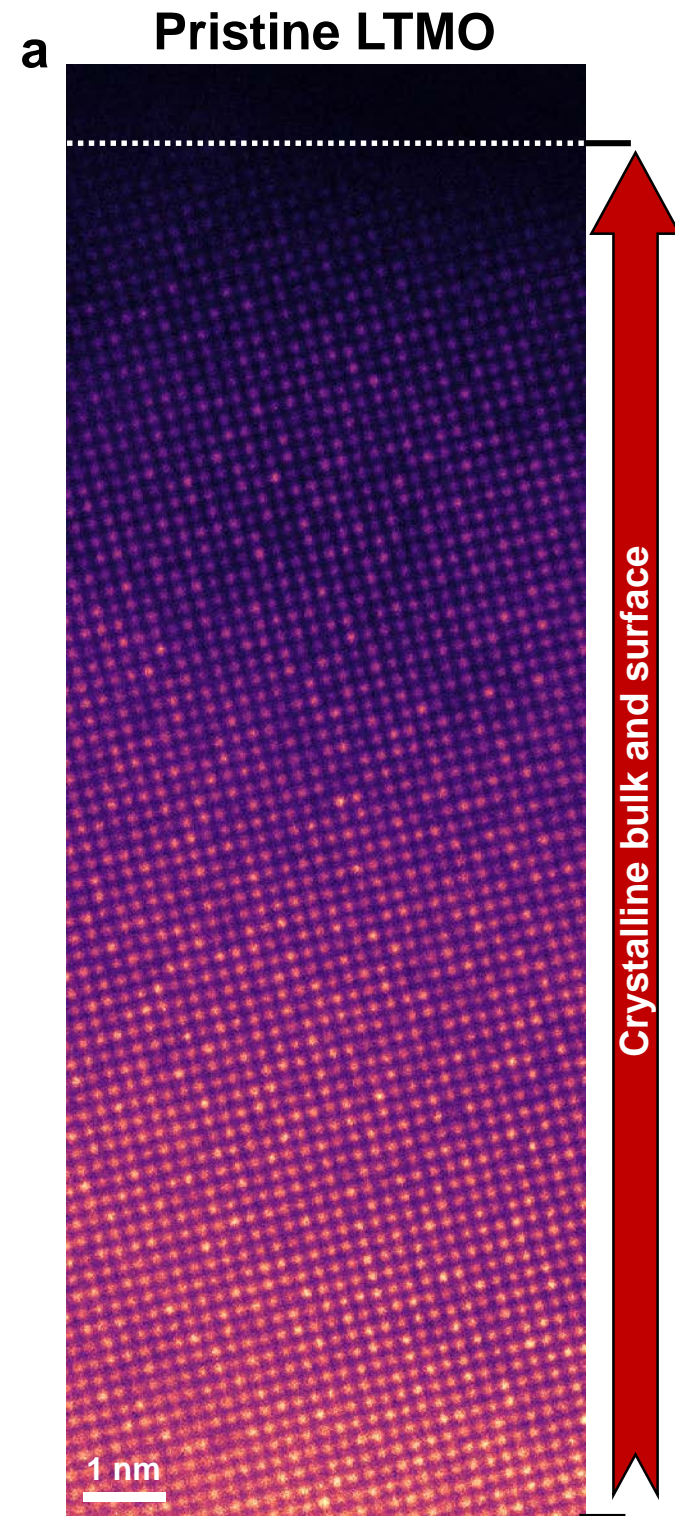
Technical Accomplishments

Bulk lattice stability of $\text{Li}_{1.2}\text{Ti}_{0.2}\text{Mn}_{0.6}\text{O}_{1.8}\text{F}_{0.2}$ upon electrochemical cycling (40 cycles)

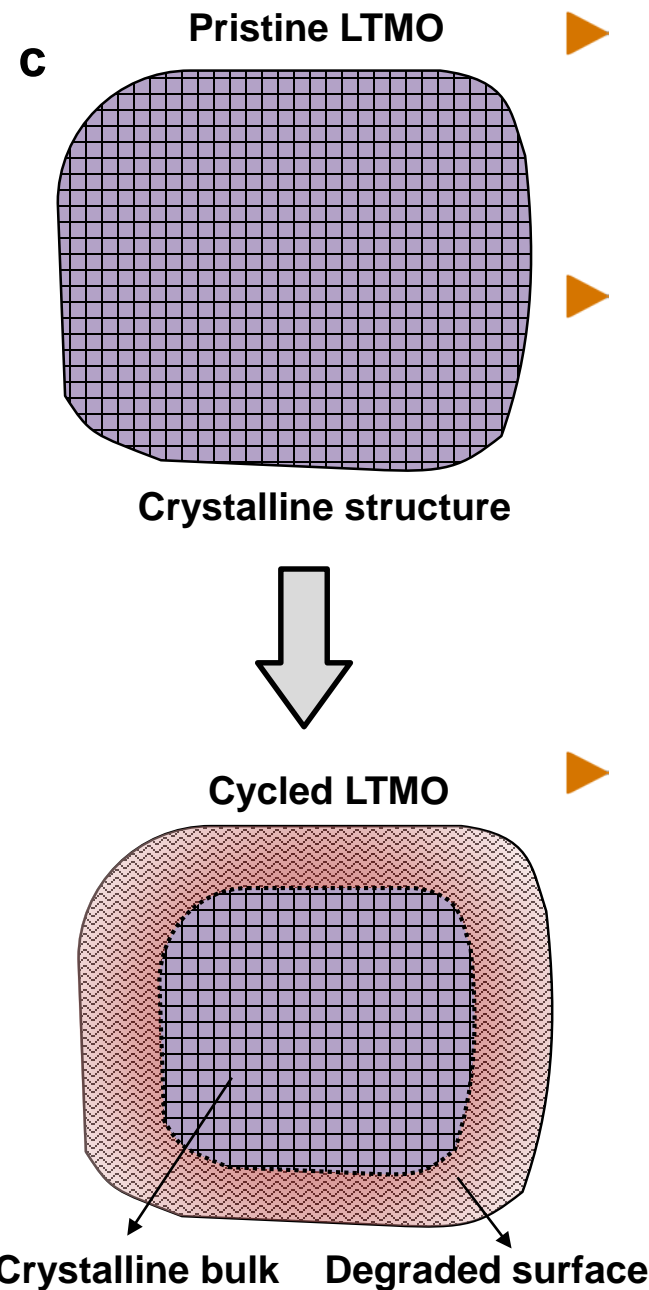


- ▶ Upon cycling of the battery, the LTMOF is subject to Mn and O loss at the surface region, while Ti does not.
- ▶ The rock-salt phase transforms to spinel structure in nanodomains.
- ▶ No elemental segregation is observed for either the rock-salt phase or the newly formed spinel phase in the cycled LTMOF.
- ▶ At the particle surface region, Ti and Mn are reduced to a low-valence state, indicating loss of oxygen near the surface region.
- ▶ In the bulk region, Ti and Mn show no reduction in the valence state.

Technical Accomplishments



Electrochemical cycling induced atomic structural evolution of LTMO ($\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ti}_{0.4}\text{O}_2$)



- ▶ For pristine LTMO, crystalline structures were observed from bulk to surface.
- ▶ Upon electrochemical cycling of the battery (after 50 cycles), while the bulk remained crystalline, the surface layer of ~10 nm in thickness was degraded.
- ▶ The surface layer degradation is indicated by void formation as a consequences of oxygen loss.

Responses to Previous Year Reviewers' Comments

- ▶ Made a poster presentation; the project was not reviewed in 2019



Collaboration and Coordination with Other Institutions

Partners:

- Lawrence Berkeley National Laboratory: Preparation of disordered rock-salt-structured cathode materials
- Argonne National Laboratory: Preparation of low-Co and Co-free cathode materials
- Oak Ridge National Laboratory: Low-Co and Co-free cathode materials, disordered rock-salt-structured cathode
- Hummingbird Scientific Inc.: Help to develop the liquid holder
- Thermofisher Scientific Inc.: *In situ* and ETEM capability development
- Battery Research Group at PNNL: Preparation of low-Co and Co-free cathode

Remaining Challenges and Barriers

- ▶ What is the structural and chemical nature of short-range order in the cation-disordered rock-salts cathode?
- ▶ How does the short-range order evolve upon battery cycling?
- ▶ How do F, O, and Li correlate in the lattice and correlate with electrochemical properties?
- ▶ How does the lattice evolve in DRX upon battery cycling?
- ▶ Which factor determines the lattice structural stability of the low-Co cathode with surface, lattice, and electrolyte modifications?
- ▶ How does grain boundary mediate mass transport affect the stability of low-Co concentration cathode and electrochemical properties?
- ▶ What is the spatial distribution and the role of a range of low-concentration dopants in low-Co cathode: Al, W and Zr?
- ▶ How does oxygen evolve in the cathode of both layered and disordered rock salt structures?
- ▶ What is the origin of the intragranular cracking in the layered cathode?

Proposed Future Work

FY2020

- ▶ Explore how the short-range order in disordered rock structure (DRX) correlates with the spatial distribution of Li, F, and O
- ▶ Reveal the surface and bulk structural and chemical evolution of disordered rock structure (DRX) upon battery cycling
- ▶ Investigate the correlation of surface and bulk lattice stability of low-Co and Co-free cathode

FY2021

- ▶ Investigate at the atomic level the spatial correlation of Li, O, and F and charge distribution in the disordered rock-salt structure
- ▶ Determine critical factors that control the stability of disordered rock-salt structure cathode
- ▶ Explore how the anionic redox function in the layer structured and rock structured cathode function
- ▶ Determine the critical factors that govern the fading mechanism of low-Co and Co-free cathode
- ▶ Establish the correlation between oxygen release and intragranular cracking in the layer structured cathode

Any proposed future work is subject to change based on funding levels

Summary

- ▶ Developed *in situ* environmental TEM method that enables us to directly probe environmental stability of cathode materials
- ▶ Revealed that water-vapor-induced Li de-intercalation is the controlling step for the formation surface passivation layer on the layer structured cathode
- ▶ The surface reaction layer shows critical thickness beyond which the surface reaction layer thickness will not increase, indicating the passivating feature of the surface reaction layer
- ▶ Tailoring the surface structure of cathode can change the critical thickness of the surface passivation layer
- ▶ Revealed that direct contact with liquid electrolyte leads to interfacial and bulk lattice instability
- ▶ Revealed the nature of the ordering in DRX: short-range order, meso-scale order, and long-range order; discovered the meso-scale ordering in DRX
- ▶ Established correlations among fabrication, ordering, and electrochemical properties for DRX

Technical Back-Up Slides



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